REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
06/07/2012	Final Technical Report	3/20/2009 - 07/31/2011

4. TITLE AND SUBTITLE

Molecular Scale Theoretical Studies of Energy Deposition and Redistribution in Crystalline High Explosives to Stimulate Enhanced Detectable Signatures

5a. CONTRACT NUMBER

5b. GRANT NUMBER

N00014-09-1-0855

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Thomas D. Sewell

5d. PROJECT NUMBER

11PR01359-02

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Sewell Research Group, Department of Chemistry
University of Missouri-Columbia
Columbia, MO 65211

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
875 North Randolph St.
Arlington, VA 22203-1995

10. SPONSOR/MONITOR'S ACRONYM(S)

ONR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; federal purpose rights.

13. SUPPLEMENTARY NOTES

20120613099

14. ABSTRACT

(Complete printed version provided with hard copies. See Final Report text.) In this project we have developed two molecular dynamics-based methods for simulating the THz-region infrared (IR) spectrum of molecular crystals. Both methods were designed for use at finite temperature and stress. The first method, referred to as the mode-relaxation approach, requires (1) the normal mode (i.e., phonon) eigenvectors and frequencies of the crystal, (2) the associated squared transition dipoles •2for all THz-region phonons with zero wave vector (k = 0), and (3) the spectral line width •for each k = 0 THz-region phonon with nonzero •2(i.e., the IR-active THz-region modes). These quantities are the ones required to specify the Lorentzian absorption profile for an individual spectral line. The eigenvectors, frequencies, and transition dipoles were obtained directly from normal mode analysis of the crystal, performed for crystal lattice parameters corresponding to a specified temperature and stress state. Line widths were determined separately for each THz mode by selectively depositing, in an otherwise thermalized crystal, a fixed amount of energy in a given

15. SUBJECT TERMS

Terahertz spectroscopy, Pentaerythritol Tetranitrate, PETN, Molecular dynamics, Vibrational energy transfer, Infrared absorption

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Dr. Thomas D. Sewell, PI
UU	UU	UU	UU		19b. TELEPHONE NUMBER *(Include area code)* 573-882-7725

INSTRUCTIONS FOR COMPLETING SF 298

1. REPORT DATE. Full publication date, including day, month, if available. Must cite at least the year and be Year 2000 compliant, e.g. 30-06-1998; xx-06-1998; xx-xx-1998.

2. REPORT TYPE. State the type of report, such as final, technical, interim, memorandum, master's thesis, progress, quarterly, research, special, group study, etc.

3. DATES COVERED. Indicate the time during which the work was performed and the report was written, e.g., Jun 1997 - Jun 1998; 1-10 Jun 1996; May - Nov 1998; Nov 1998.

4. TITLE. Enter title and subtitle with volume number and part number, if applicable. On classified documents, enter the title classification in parentheses.

5a. CONTRACT NUMBER. Enter all contract numbers as they appear in the report, e.g. F33615-86-C-5169.

5b. GRANT NUMBER. Enter all grant numbers as they appear in the report, e.g. AFOSR-82-1234.

5c. PROGRAM ELEMENT NUMBER. Enter all program element numbers as they appear in the report, e.g. 61101A.

5d. PROJECT NUMBER. Enter all project numbers as they appear in the report, e.g. 1F665702D1257; ILIR.

5e. TASK NUMBER. Enter all task numbers as they appear in the report, e.g. 05; RF0330201; T4112.

5f. WORK UNIT NUMBER. Enter all work unit numbers as they appear in the report, e.g. 001; AFAPL30480105.

6. AUTHOR(S). Enter name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. The form of entry is the last name, first name, middle initial, and additional qualifiers separated by commas, e.g. Smith, Richard, J, Jr.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES). Self-explanatory.

8. PERFORMING ORGANIZATION REPORT NUMBER. Enter all unique alphanumeric report numbers assigned by the performing organization, e.g. BRL-1234; AFWL-TR-85-4017-Vol-21-PT-2.

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES). Enter the name and address of the organization(s) financially responsible for and monitoring the work.

10. SPONSOR/MONITOR'S ACRONYM(S). Enter, if available, e.g. BRL, ARDEC, NADC.

11. SPONSOR/MONITOR'S REPORT NUMBER(S). Enter report number as assigned by the sponsoring/ monitoring agency, if available, e.g. BRL-TR-829; -215.

12. DISTRIBUTION/AVAILABILITY STATEMENT. Use agency-mandated availability statements to indicate the public availability or distribution limitations of the report. If additional limitations/ restrictions or special markings are indicated, follow agency authorization procedures, e.g. RD/FRD, PROPIN, ITAR, etc. Include copyright information.

13. SUPPLEMENTARY NOTES. Enter information not included elsewhere such as: prepared in cooperation with; translation of; report supersedes; old edition number, etc.

14. ABSTRACT. A brief (approximately 200 words) factual summary of the most significant information.

15. SUBJECT TERMS. Key words or phrases identifying major concepts in the report.

16. SECURITY CLASSIFICATION. Enter security classification in accordance with security classification regulations, e.g. U, C, S, etc. If this form contains classified information, stamp classification level on the top and bottom of this page.

17. LIMITATION OF ABSTRACT. This block must be completed to assign a distribution limitation to the abstract. Enter UU (Unclassified Unlimited) or SAR (Same as Report). An entry in this block is necessary if the abstract is to be limited.

Molecular Scale Theoretical Studies of Energy Deposition and Redistribution in Crystalline High Explosives to Stimulate Enhanced Detectable Signatures

Thomas D. Sewell
Department of Chemistry; University of Missouri-Columbia; Columbia, MO 65211-7600

In this project we have developed two molecular dynamics-based methods for simulating the THz-region infrared (IR) spectrum of molecular crystals. Both methods were designed for use at finite temperature and stress. The first method, referred to as the *mode-relaxation approach*, requires (1) the normal mode (*i.e.*, phonon) eigenvectors and frequencies of the crystal, (2) the associated squared transition dipoles μ^2 for all THz-region phonons with zero wave vector ($\mathbf{k} = 0$), and (3) the spectral line width γ for each $\mathbf{k} = 0$ THz-region phonon with nonzero μ^2 (*i.e.*, the IR-active THz-region modes). These quantities are the ones required to specify the Lorentzian absorption profile for an individual spectral line. The eigenvectors, frequencies, and transition dipoles were obtained directly from normal mode analysis of the crystal, performed for crystal lattice parameters corresponding to a specified temperature and stress state. Line widths were determined separately for each THz mode by selectively depositing, in an otherwise thermalized crystal, a fixed amount of energy in a given normal mode and monitoring the time dependence of energy transfer from that mode. Relaxation time constants for each mode were determined by fitting the corresponding energy decay time history, averaged over an appropriate ensemble of trajectories, to an exponential function; from which the line width was obtained using $\gamma = 1/(4\pi c\tau)$. The Lorentzian profiles for the IR-active modes were summed to yield the absorption spectrum. The advantages of the mode-relaxation approach are that it yields (1) detailed information concerning which particular normal modes contribute to the THz absorption intensity and (2) time scales and pathways for energy transfer from the selectively excited THz modes into the remaining modes of the system.

In the second method, referred to as the *DDACF approach*, the IR absorption intensity is obtained as the Fourier transform of the dipole-dipole autocorrelation function of the crystal calculated from an ensemble of equilibrium trajectories for a given pressure and temperature. In contrast to the mode-relaxation approach, the DDACF approach does not provide information about particular mode-mode energy transfer pathways. It does, however, sample directly the effective modes of the system, as opposed to the set of zeroth-order normal modes obtained from normal mode analysis, at any temperature or for any defect structure in the crystal.

Both methods were evaluated by predicting the THz spectrum of the secondary explosive pentaerythritol tetranitrate (PETN) for a variety of thermodynamic conditions. Specifically, using a force field known to accurately predict several thermodynamic and mechanical properties of crystalline PETN, simulations were performed for defect-free crystals at T = 298 K and hydrostatic pressures of P = 0, 1, 2, and 3 GPa. Simulations were also performed at T = 298 K and P = 0 GPa for crystals containing vacancy defects. Additional studies were performed for defect-free crystals at T = 298 K and P = 0 GPa to assess the sensitivity of the predictions to modest modifications of the force field model; namely, replacement of harmonic oscillator covalent bond-stretching terms by Morse oscillators, or application of geometric constraints to fix C-H and N-O covalent bond distances at the corresponding equilibrium values. Both methods predict IR spectra at T = 298 K and P = 0 GPa that are in good agreement with experimental data, although the predicted peak widths are noticeably narrower than the observed ones. There are no high-pressure data available for direct comparison. However, the predicted THz-region IR pressure coefficients $d\omega/dP$ agree well with Raman data obtained for slightly higher frequencies. The two principal effects of vacancy defects on the predicted spectra are red shifting of the main absorption peaks and broad, increased absorption intensity at the lower end of the frequency range.

Total Funding
$203,650

Dates of Performance:
03/20/2009 –07/31/2011

Personnel Supported:
Prof. Thomas D. Sewell
Dr. Andrey Y. Pereverzev, Postdoctoral Research Fellow
Mr. Reilly M. Eason: Graduate Research Assistant

Publications:

A molecular dynamics simulation study of crystalline 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) as a function of pressure and temperature, Dmitry Bedrov, Oleg Borodin, Grant D. Smith, and Thomas D. Sewell, Lewis L. Stevens, and Dana M. Dattelbaum, Journal of Chemical Physics **131**, 224703 (2009).

Terahertz spectrum and normal-mode relaxation in pentaerythritol tetranitrate: Effect of changes in bond-stretching force field terms, Andrey Pereverzev and Thomas D. Sewell, Journal of Chemical Physics **134**, 224502 (2011).

Terahertz spectrum and normal-mode relaxation in pentaerythritol tetranitrate: Pressure effects between 0 and 3 GPa, Andrey Pereverzev and Thomas D. Sewell, Chemical Physics Letters **515**, 32 (2011).

(Refereed Conference Proceeding) *Effect of Vacancy Defects on the Terahertz Spectrum of Crystalline Pentaerythritol Tetranitrate,* Andrey Pereverzev and Thomas D. Sewell, to appear in Proceedings of the 2011 APS Topical Conference on Shock Compression of Condensed Matter, Chicago, IL, 26 June – 1 July 2011.

Conferences and other presentations where research supported by this project was highlighted:

Thomas D. Sewell (Invited Lecturer), Institute of Shock Physics (Imperial College London) – Symposium on Energetic Materials; 1-3 February 2012; London, England.

Thomas D. Sewell (Invited Workshop Participant), Advanced Multifunctional Energetic Materials; 12-13 October 2011; University of Illinois, Urbana, IL.

Thomas D. Sewell (Invited Speaker), Office of Naval Research Workshop on Mechanisms and Effects of Energy-Coupling Waves (e/m and acoustic) into Explosive Composite Compounds to Stimulate Signatures; Virginia Beach, VA; 16-17 June 2010.

Thomas D. Sewell (Invited Speaker), Gordon Research Conference on Energetic Materials; Tilton, NH; 13-18 June 2010.

Thomas D. Sewell (Invited Speaker), New Models and Hydrocodes for Shock Wave Compression in Condensed Matter; Paris, France; 24-28 May 2010.

Andrey Pereverzev (Invited Speaker), *Investigation of terahertz spectra of crystalline energetic materials: Molecular dynamics approaches*, Workshop on Chemistry at Extreme Conditions; Santa Fe, NM; 18-20 January 2012.

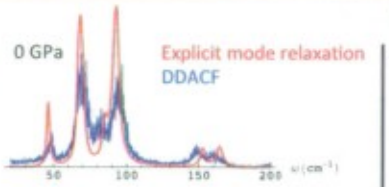
Andrey Pereverzev (Invited Speaker), *Theoretical Studies of THz Spectroscopy and Dynamics in Crystalline Pentaerythritol Tetranitrate*, DyNAMITE Chemistry Departmental Seminar, University of Missouri, 6 September 2011.

Andrey Pereverzev and **Thomas D. Sewell** (Contributed Talk), *Molecular dynamics study of normal mode relaxation and infrared spectra in pentaerythritol tetranitrate*, 2011 APS Topical Conference on Shock Compression of Condensed Matter (29 June – 2 July 2011, Chicago, IL).

Molecular Scale Theoretical Studies of Energy Deposition and Redistribution in Crystalline High Explosives to Stimulate Enhanced Detectable Signatures 6.1

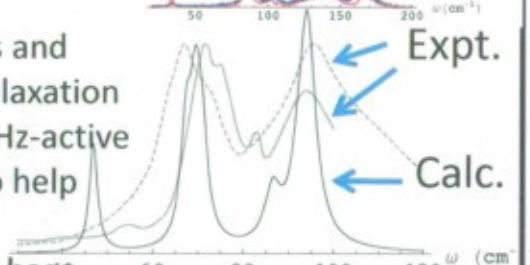
RESEARCH QUESTION

- Is it possible to localize sufficient energy by THz or ultrasonic excitation to enhance existing signatures or create a new ones in an explosive material?



OBJECTIVE

- Determine the pathways and time scales for energy relaxation following excitation of THz-active modes in PETN crystal to help provide the required fundamental knowledge base.



CHALLENGES

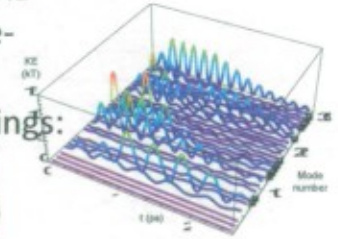
- Lack of fundamental knowledge concerning THz spectra in explosive crystals; preceding models have either been developed for 0 K or by using empirical line widths to fit data.
- Defining a suitable orthonormal basis given non-negligible thermal expansion (0K → 300 K) and importance of "floppy" modes; applicability of the classical approximation.
- Interpreting experimental data in light of wide sample-to-sample variation depending on sample purity & preparation.
- Incorporating defects (vacancies, voids, interfaces) in ways sufficiently realistic to avoid ridiculous finite-size effects.
- Adapting normal mode basis descriptions for defective/inhomogeneous systems.

TECHNICAL APPROACH:

- **Study PETN** crystal initially: polyatomic HE, good data available; use MD with a validated force field.
- **Obtain eigenvectors**, frequencies, and transition dipoles for phonon modes using normal mode analysis. **Identify** IR-active modes based on the transition dipoles. **Selectively excite** individual THz modes to determine mode-by-mode spectral line widths. **Combine** the preceding in a quantum mechanical expression to predict the THz-region IR absorption spectrum.
- **Study relaxation** pathways for individual modes.
- **Calculate THz IR absorption** from Fourier transform of dipole-dipole autocorrelation function (DDACF).
- **Consider effects** of pressure, defects, and force field.

ACCOMPLISHMENTS

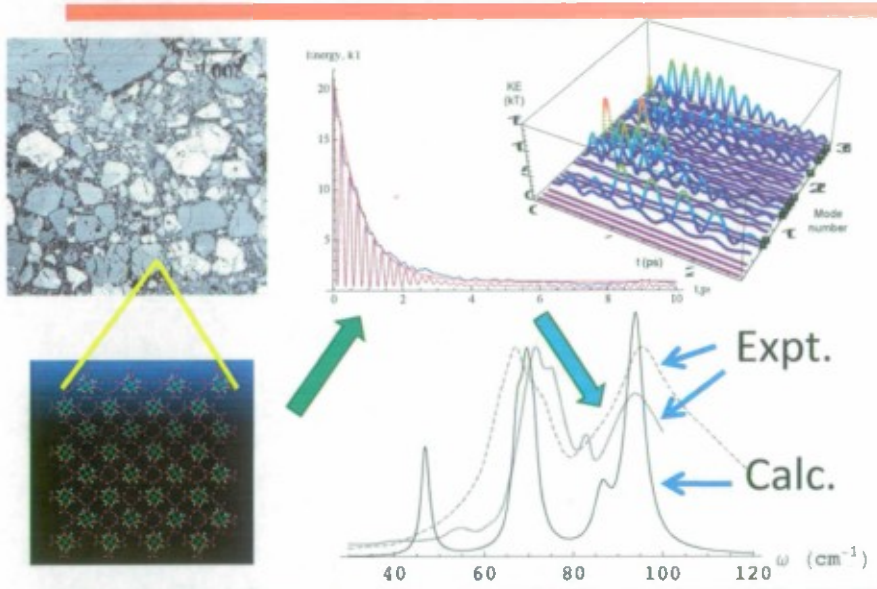
- Successfully completed all objectives listed at left, including *parameter-free prediction of THz absorption spectrum for PETN* and mode-specific relaxation pathways.



- Three journal publications, one proceedings:
  - J. Chem. Phys. 134,014513 (2011)
  - J. Chem. Phys. 134, 244502 (2011)
  - Chem. Phys. Letters (in press 9/11)
  - APS shock conference proceedings (accepted).
- Three Invited Talks; one contributed (New Models, Gordon Conference, PacifiChem; APS shock conference).
- One U.S. Citizen postdoc (Andrey Pereverzev, 10/09-) and one U.S. Citizen GRA supported (Reilly Eason, Fall '09).

Thomas D. Sewell (PI), Department of Chemistry, University of Missouri-Columbia, (573)-882-7725, sewellt@missouri.edu

Molecular Scale Theoretical Studies of Energy Deposition and Redistribution in Crystalline High Explosives to Stimulate Enhanced Detectable Signatures 6.1



RESEARCH QUESTIONS:

- Is it possible to localize sufficient energy in a HE material by THz or ultrasonic excitation to enhance existing detectable signatures, create new ones, or even disable a device?
- More fundamentally: What are the pathways and time scales for energy redistribution following selective excitation of THz-active modes in molecularly complex materials?
- How can information calculated or measured on atomic and mesoscopic scales be combined synergistically to yield improved predictive capability in multi-physics phenomena?
- Can predictions from atomic-scale methods be used to interpret data or discriminate between conflicting data sets?

TECHNICAL APPROACH:

- **Study PETN** crystal initially: polyatomic HE, good data available; use MD with a validated force field.
- **Obtain eigenvectors**, frequencies, and transition dipoles for phonon modes using normal mode analysis. **Identify** IR-active modes based on the transition dipoles. **Selectively excite** individual THz modes to determine mode-by-mode spectral line widths. **Combine** the preceding in a quantum mechanical expression to predict the THz-region IR absorption spectrum.
- **Study relaxation** pathways for individual modes.
- **Calculate THz IR absorption** from Fourier transform of dipole-dipole autocorrelation function.
- **Consider effects** of pressure, defects, and force field.

SCHEDULE (Two-Year Project):

TASKS	FY09	FY10	FY11
Search for/hire Postdoctoral Scholar; Dr. Andrey Pereverzev started 10/2009			
Implement PETN force field and validate; obtain phonon eigenvectors &			
Determine THz-active modes; develop THz excitation scheme; perform simulations			
Predict THz spectrum based on calculated transition dipoles & line widths			
Study effects of temperature, density, & defects on calculated spectra; consider additional approaches for simulating spectra			

Thomas D. Sewell (PI), Department of Chemistry, University of Missouri-Columbia, (573)-882-7725, sewellt@missouri.edu